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Succinylated rice bran starch as adsorbent of heavy metals in aqueous solution

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ABSTRACT:

In this study, starch was prepared and modified from rice bran as abundant and cheap raw material. Its adsorption efficiency against heavy metals in aqueous solutions was determined. Desorption, recovery of heavy metals and recyclability of the adsorbent were also calculated based on desorption efficiency and degradability of the adsorbent determined through repeated process of adsorption-desorption. Based on the results of the study, 39.3% of starch was extracted and modified from rice bran. Copper ions were adsorbed with 97.7%, cadmium ions with 95.9% and lead ions with 80.5% efficiency at 25°C. and pH 7.0. The adsorbent best fitted the Langmuir isotherm with maximum adsorption capacity of 195.44 mg/g. Repeated cycles of adsorption and desorption posed minimal decrease in the adsorption efficiency offering the advantage of recovering both the adsorbent and heavy metals, thus reducing its presence and adverse health effects promoting green chemistry.

Keywords:

Rice starch, Succinylation, Heavy metal, Adsorption isotherm, Rice bran.

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INTRODUCTION

Philippines is naturally surrounded by different water bodies. Despite this relative abundance in water, 16 million Filipinos in 432 municipalities do not have access to safe drinking water. Thus, clean water remains a precious and often scarce commodity. The wide range of contaminants present in various water sources are due to industrialization, mismanagement of agricultural and domestic wastes, etc. Among these contaminants, heavy metals, such as lead, copper, and cadmium, are some of the major concerns in environmental pollution and water consumption due to their toxicity and adverse health effects (Sankhla *et al*., 2016).

Currently, methods such as chemical precipitation, coagulation-flocculation, flotation, membrane filtration, and adsorption are used to minimize heavy metal contamination (Gunatilake, 2015). According to Tripathi and Ranjan (2015), among these treatment methods, adsorption has emerged out as the most economical and effective. Adsorption involves the adherence of a substance to the surface of a liquid or solid through physical and/or chemical means. However, similar with other methods, it also has some limitations (Dong *et al*., 2010). Most of the adsorbents, though deemed effective, that are used today are either non-biodegradable/recyclable or expensive, such as the utilization of activated carbon (Zhang *et al*., 2014). Thus, studies focusing on the utilization of biodegradables, such as agricultural materials and forest waste products, as adsorbents of heavy metals have been conducted.

Recently, there is a rise in using starch as a biodegradable raw material in many industries, from biocomposites to adsorbents. Starch, is a cheap, biodegradable and abundantly available biopolymer that has many applications in food and non-food industries (Alcázar-Alay and Meireles, 2015). However, on its native form Haroon *et al*. (2016) stated that there are limitations in using native starch as an adsorbent such as changes in physicochemical properties upon application of heat and the absence of molecular groups responsible for the adsorption for dyes and heavy metals. In order to make native starch capable of adsorbing heavy metals and dyes, modification using different active groups with adsorption activity (such as amine phosphate and esters like maleic acid and succinic anhydride) may be done (BeMiller and Whistler, 2009; Lin *et al*., 2012; Ma *et al*., 2015; Sancey *et al*., 2011; Soto *et al*., 2016). In comparison to other cereal starches, starch from rice is currently more expensive (Fabian, 2011). Thus, the possibility to find other sources of rice starch, like rice bran, would be advantageous.

One source of relatively inexpensive starch is rice bran, an underutilized byproduct of rice polishing, as most of it is used in animal feed and fuel. In this study, starch was prepared and modified from rice bran. Its adsorption efficiency against heavy metals was determined. Degradation of the adsorbent upon undergoing cycles of adsorption-desorption as well as recovery of heavy metals were also investigated to further evaluate the use of the synthesized product.

MATERIALS AND METHODS

Isolation of rice starch from rice bran

Starch from rice bran was extracted through wet -milling method described by Fabian *et al*. (2011) using 10 g of sample. The bran was soaked in 50 mL of water for three hours. The mixture was then blended for five minutes to homogenize using a blender and screened using a cheese cloth. It was blended and screened twice using 50 mL 70% Ethanol (EtOH) in the 2nd cycle and 50 mL 0.1M NaOH in the 3rd, collecting the filtrate after

Table 1. Percentage of Succinyl and degree of substitution of rice bran starch

S. No	Sample name	Succinyl %	Degree of substitution
1	Native RB Starch	0%	0
2	SS1	2.50%	0.55
3	SS2	4.94%	1.63
4	SS3	6.48%	3.12

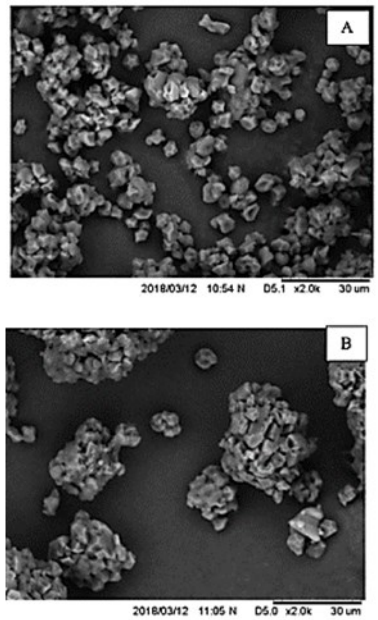

Figure 1. Scanning electron micrographs of (a) native RBS and (b) SS3 at x 2,000 magnification

being centrifuged for 15 min. The residue was then added with 100 mL water, making a slurry and was filtered in a cheese cloth. The collected filtrate was filtered again in a Whatman filter paper no. 42 (2.5 µm) and washed with 20 mL water, 40 mL 0.1 NaOH, and lastly with 40 mL water, successively. The obtained residue was dried in an oven at 55°C for six hours.

Modification of Rice Bran Starch (RBS)

The method used by Awokoya and Moronkola (2012) was used with slight modification. About 100 g of starch was dispersed in 300 mL distilled water and stirred for one hour. The pH of the resulting slurry was adjusted to 9.0 using 1M NaOH. Then, 5, 10 and 15 g of succinic anhydride were added to the starch slurry and stirred over a period of two hours while maintaining the pH range of 8.0-9.0 by constant stirring and 1M NaOH or 1M HCl, were added to maintain the alkalinity. After two hours, the pH was adjusted to pH 6.0 using 0.5 M HCl. The mixture was filtered and washed using Whatman filter paper no 42 (2.5 µm) for six times and then oven-dried at 55°C for six hours.

Determination of degree of succinylation

In a conical flask, one gram of the modified and native starch (for blank) was added along with 50 mL of 75% EtOH, and the mixture was refluxed at 50°C for 30 min. After reaching room temperature, 40 mL of 0.5 M NaOH was added and the mixture was allowed to stand for seventy two hours with occasional shaking. The excess alkali was determined by titration with 0.5 M HCl using phenolphthalein indicator (Bhandari and Singhal, 2002). The percentage of succinyl group present and the Degree of Succinylation (DS) of each sample were calculated using the equations based on the study of Lawal (2012):

$$\%Succinyl = \frac{(blank_{titre} - sample_{titre})\ x\ 0.1\ x\ M_{acid}\ x\ 100}{wt.\ of\ sample} \quad (1)$$

$$DS = \frac{162\ x\ \%_{succinyl}}{1000 - (99\ x\ \%_{succinyl})} \quad (2)$$

Surface morphology analysis

The surface morphology and size of modified and native starches were determined using Scanning Electron Microscopy (SEM) and Hitachi TM3000 Tabletop Microscope as shown in Figure 1.

Adsorption experiments

The modified starch having the highest degree of modification was selected (as the higher the degree of substitution, the higher the adsorption capacity) to be used as the adsorbent of Pb^{2+}, Cu^{2+} and Cd^{2+}. The method used by Awokoya and Moronkola (2012) was used via batch technique with slight modification. A 100 mg

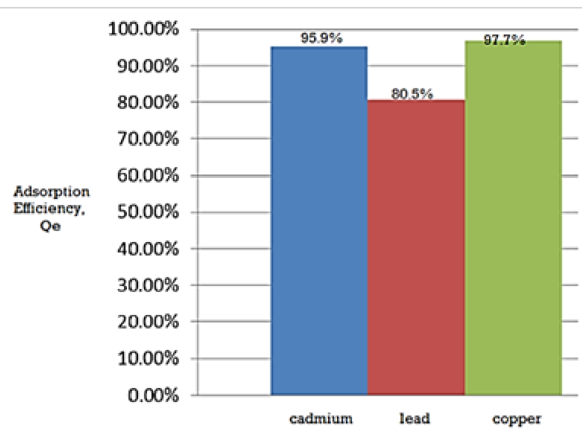

Figure 2. Adsorption efficiency of adsorbent against different heavy metals

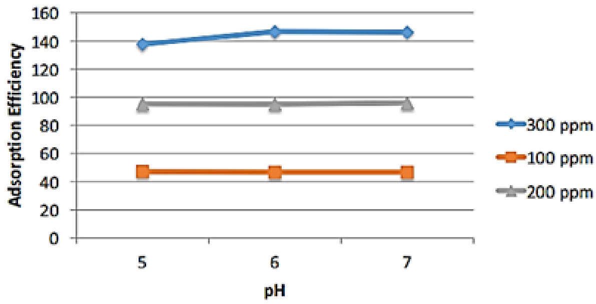

Figure 3. Adsorption efficiency of SS3 in different cadmium ion concentrations at varying pH

of the modified starch was added to a 50 mL of an aqueous solution of $Pb(NO_3)_2$, $Cu(NO_3)_2$, and $Cd(NO_3)_2$ with varying concentrations of 100, 200 and 300 ppm.

For the pH parameters, the initial pH was adjusted from 5.0, 6.0 and 7.0 using 0.1M HNO_3 or 0.1M NaOH prior to the addition of adsorbent. For the temperature parameters, the temperature of the solutions containing the adsorbent was adjusted to the desired temperatures of 25°C, 35°C and 45°C. For the determination of the adsorption efficiency, the initial and the residual/final metal concentrations were used in the calculation of the adsorption quantity (Qe, mg/g) using the equation based on the study of Awokoya and Moronkoya (2012):

$$Q_e = \frac{V\,(C_o - C_e)}{M} \qquad (3)$$

Where: Qe - adsorption efficiency; V - volume of the solution; Co - initial metal concentration; Ce - final metal concentration and M - weight of the adsorbent.

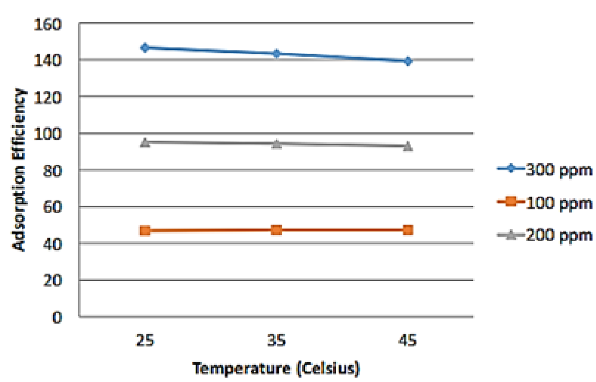

Figure 4. Adsorption efficiency of SS3 in different Cd ion concentrations at varying temperatures

Adsorption isotherm studies

The initial and final concentrations of the metals from the parameters were then used to determine the equilibrium data/adsorption isotherm. The adsorption isotherms of Cd^{2+} were evaluated using the Langmuir and the Freundlich model.

Desorption experiments, recovery of metals and repeated Use

To determine if the modified starch is reusable, the method conducted by Awokoya and Moronkola (2012) was used with some modifications. The adsorption-desorption method was repeated for three cycles, with the initial concentration of 100 ppm at pH=6 and 25^0C. The heavy metal-loaded adsorbent was added into a beaker containing 100 mL of 1% (v/v) HNO_3 solution for 30 min at room temperature. Then, the mixture was centrifuged for five min and the adsorbent was removed. The desorption efficiency was calculated using the equation based on the study of Awokoya and Moronkola (2012);

$$DE = \frac{C_t\, x\, V}{M_o} x\, 100\% \qquad (4)$$

Where: Ct (mg/L) - concentration of the metal ions in the desorption solution; V - volume of the desorption solution and Mo (g) is the amount of metal ions adsorbed.

The recovery of metals was conducted after finishing all of adsorption/desorption experiments. The resulting heavy metal-loaded solution was treated with 1M NaOH, adjusting first and maintaining the pH levels (following the solubility curve) to produce metal hydroxides. The precipitates were then filtered and dried at 105°C for an hour.

RESULTS AND DISCUSSION

Extraction and Isolation of RBS

Rice Starch (RS) isolated from its bran via wet-milling process yielded 39.3%. The source of the rice bran used in this study was NSIC Rc222, a rice variety

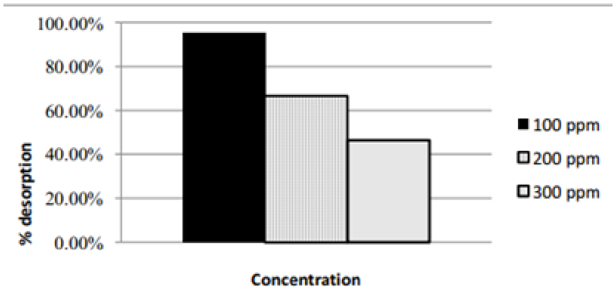

Figure 5. Percent desorption of SS3 in different Cd ion concentrations

with an intermediate classification of amylose.

Modification via succinylation

The degree of substitution was controlled by the addition of succinic anhydride (5, 10 and 20 g), producing three kinds of Succinylated Starch (SS), assigned as SS1, SS2, and SS3, respectively (Table 1). The degree of substitution values and percentage of succinyl increased with the increase of concentration of succinic anhydride. The increase in succinic anhydride concentration favors the production of starch succinate. Due to this, the sample with the highest degree of substitution, SS3, was used for the succeeding studies.

Surface morphology of native and modified RBS

Succinylation of RBS caused drastic changes in the surface and less definition on the edges of the starch granules compared to the native one. Similar observations were noted in yam (Lawal, 2012), cassava Ekebafe *et al*., 2015) and cornstarch (Awokoya and Moronkola, 2012). The average particle size/diameter of the native RBS observed was 1.8 µm, while SS3 was 1.7µm.

Table 2. Adsorption isotherm model for SS3 against Cd^2

Freundlich adsorption isotherm model							
Temp Exp. (at 100, 200, 300 ppm)				pH Exp. (at 100, 200, 300 ppm)			
Concentration (ppm)	Temperature (◦C)	r^2	qm*KL	Concentration (ppm)	pH	r^2	qm*KL
100	25	0.9559	0.600853	100	5	0.8552	0.596944
	35				6		
	45				7		
200	25	0.9731	0.504286	200	5	0.5587	0.50597
	35				6		
	45				7		
300	25	0.0485	0.461979	300	5	0.7087	0.469373
	35				6		
	45				7		

Langmuir isotherm							
Temp Exp. (at 100, 200, 300 ppm)				pH Exp. (at 100, 200, 300 ppm)			
Concentration (ppm)	Temperature (◦C)	r^2	qm*KL	Concentration (ppm)	pH	r^2	qm*KL
100	25	0.9697	14.97006	100	5	0.8702	11.08647
	35				6		
	45				7		
200	25	0.9429	37.03704	200	5	0.8885	36.36364
	35				6		
	45				7		
300	25	0.9659	85.47009	300	5	0.9907	83.33333
	35				6		
	45				7		

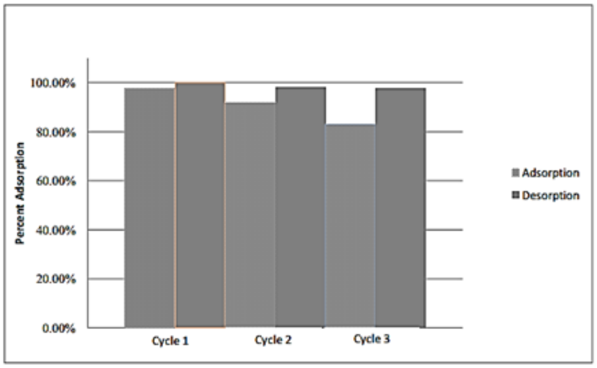

Figure 6. Sorption cycles of SS3

Adsorption experiments

Preliminary evaluation of heavy metal adsorption

The adsorption efficiency of SS3 in 100 ppm of Pb^{+2}, Cd^{+2}, and Cu^{+2} was presented in terms of constant pH (6) and temperature (25^0C) (Figure 2). The synthesized adsorbent has adsorbent efficiency above 50% against the three heavy metals. This suggests that the adsorbent is not selective and not specific. The adsorption data obtained is plotted at varying pH and concentrations as shown in Figure 3. The adsorbed amount of heavy metal by SS3 was dependent on the initial heavy metal concentration and pH. The adsorption efficiency of SS3 increases along with the increase in the initial concentration of cadmium and pH. The increased Cd^{+2} adsorption may be explained by the ionization of the reaction sites on the surface of the adsorbent at increasing pH, which involves reaction of protonation and binding (Awokoya and Moronkola, 2012).

The adsorption data obtained is plotted at varying temperature and concentrations as shown in Figure 4. The adsorbed amount of heavy metal by SS3was dependent on the initial heavy metal concentration and the temperature of the solution. The decreasing Cd^{+2} adsorption efficiency may be explained by the weakening of the reaction sites between the adsorbent and the heavy metal ions, which involves physisorption and indicated the process is exothermic.

Figure 7. Recovered HM hydroxide of lead (left), copper (middle) and cadmium (right)

Desorption experiments

Effect of initial concentration to percent desorption Figure 5 shows the percent desorption in different initial concentrations of Cd^{+2}. As the initial concentration increases, the ability for the SS3 to undergo desorption decreases, similar with the desorption of heavy metal ions using acid such as HCl (Moyo *et al*., 2013).

Adsorption isotherms

The adsorption isotherm of SS3 was described using Langmuir and Freundlich adsorption models (Reed and Matsumoto, 1993). The results are shown in Table 2. The adsorption process was best described by the Langmuir Isotherm model, having an initial heavy metal concentration of 300 ppm, at pH 7 and 25^0C. This isotherm model considers the balance of relative rates of adsorption and desorption and thus, the surface coverage (Ayawei *et al*., 2017). It was determined to have a maximum adsorption concentration calculated as 195.44 mg of heavy metal per gram of adsorbent (mg/g).

Adsorbent reusability and heavy metal recovery

The –sorption cycle data obtained was plotted at an initial concentration of 100 ppm, pH 6 and 25^0C as shown in Figure 6. There was a slight decrease in the heavy metal uptake/adsorption and desorption efficiencies after every cycle. It may be due to some loss in the amount of adsorbent, saturation of heavy metal ions, and the possibility of material degradation due to the acid used in the desorption process (Mata *et al*., 2010). As for the heavy metal recovery as a waste treatment procedure, the desorption solution, along with the remaining standard series containing heavy metals, were treated with 1M NaOH to produce hydroxides (following the solubility curve). Recovered heavy metals were in the form of hydroxide salts (Figure 7). The copper hydroxide recovered turned into black due to oxidation.

CONCLUSION

Succinylation of starch from rice bran has been shown to be an efficient biodegradable material for adsorbing heavy metals from aqueous solutions. The modified starch is capable of repeated use without considerable loss of adsorption capacity. Thus, as a biodegradable, cheap and effective adsorbent, the modified starch may pose an advantage.

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DECLARATION OF CONFLICTING INTERESTS

No potential conflicts of interest may arise with respect to the research, authorship, and/or publication of this article.

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